

IN-SITU SMALL-ANGLE X-RAY SCATTERING STUDY OF CRYSTALLIZATION IN POLY(ETHYLENE/HEXENE) COPOLYMER SUBJECTED TO STEP SHEAR

Zhigang Wang¹, Howard Wang¹, Benjamin S. Hsiao², Dilip Gersappe³ and Charles C. Han¹

¹Polymers Division, National Institute of Standards and Technology
Gaithersburg, MD, 20899

²Department of Chemistry, State University of New York at Stony Brook
Stony Brook, NY, 11794

³Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, NY 11794

Introduction

There have been intense renewal scientific and technological interests in polyolefins and polyolefin blends since the innovation of metallocenes catalysts in the past decade.^{1,2} The metallocene-based polyolefins have substantially narrower molecular mass distributions and more controlled chain architecture or stereospecificity than the materials produced from conventional heterogeneous Ziegler-Natta catalysts.^{3,4} As the final properties of polyolefins are affected by chemical composition, chain architecture, crystal structure, morphology and processing, systematic studies on statistical polyethylene copolymers and blends of two polyolefins: poly(ethylene-co-hexene) (PEH) and poly(ethylene-co-butylene) (PEB), have been carried out in our group. In the blend system, simultaneous occurrences of crystallization and liquid-liquid phase separation can lead to a complicated morphology.^{5,6} Based on knowledge of the competition of liquid-liquid phase separation and crystallization in quiescent state of the blends, we recently performed the step shear induced crystallization study by time-resolved synchrotron small-angle X-ray scattering (SAXS) technique. In this paper, we reported the results of crystallization in PEH, one component of the blends, subjected to the controlled step shear.

Experimental*

PEH was supplied by ExxonMobil Chemical Company. It had a mass-average molecular mass, M_w , of 110,000 g/mol.* The content of hexane in PEH was ≈ 3 mole %. The branch density was about 1 branch per 57 backbone carbons. The melting point of PEH was ≈ 127 °C determined by Perkin-Elmer differential scanning calorimetry (DSC7) instrument using the heating rate of 10 °C/min.* The sample was melt-pressed into a disc with thickness between 0.5 mm and 1.0 mm and then cut into the shape of a ring with the inner diameter of 10 mm and the outer diameter of 20 mm.

A controlled shear-field and thermal history were applied to the PEH sample by using a Linkam CSS-450 high temperature optical shearing stage, which had been modified for the *in-situ* X-ray scattering measurements. Time-resolved two-dimensional small-angle X-ray scattering measurement using a MAR CCD X-ray detector was performed at the Advanced Polymers Beamline (X27C) in National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL).* The detailed experimental setup for SAXS and the high temperature shearing stage have been described in previous publications.^{7,8} It is worth noting that the sample temperatures during our experimental procedures were well calibrated through the standard samples. The uncertainty of temperatures in this study was 1 °C.

The experimental procedures are as follows. The sample was heated to 160 °C, held for 5 min and then cooled to 115 °C at a rate of 30 °C/min. As the instrument reached the setting temperature, an additional waiting time of 1 min was used to assure that the sample truly reached 115 °C. After 2 min crystallization time at 115 °C, a step shear with the rate of 60 s⁻¹ and the strain of 2000 % was applied to the sample. The duration of the shear was 0.33 s. Time-resolved SAXS measurement was performed with a data acquisition time of 15 s per scan. The sample-to-detector distance used was 1568 mm. The crystallization of PEH under the same thermal conditions without being sheared was recorded at first for comparison.

Results and Discussion

* The references to commercial equipment or materials do not imply recommendation or endorsement by the National Institute of Standards and Technology.

Figures 1 and 2 illustrate a series of SAXS patterns of PEH during isothermal crystallization at 115 °C without and with step shear, respectively. The patterns in Figure 1 are completely isotropic. The integrated scattering intensity is found to increase with time, which reflects the process of crystallization. The integrated SAXS intensity from each image shows a diffuse scattering profile. However, the Lorentz-corrected profile indicates a distinct scattering peak (Figure 3a). From the peak position, the long period of lamellar stacks (≈ 350 Å) in PEH can be estimated by using the Bragg law ($L_B = 2\pi/q$, here q is the scattering vector). This result is consistent with our previous observations in PEH crystallized at 115 °C by optical microscopy, atomic force microscopy (AFM), and transmitted electron microscopy (TEM), which exhibited the formation of lamellar stacks in sheaf-like spherulitic morphology.⁹ The overall correlation of the lamellae in PEH at 115 °C is relatively poor, which leads to the observation of diffuse scattering in the raw patterns, even though the sample has been isothermally crystallized for a long time (> 7 h). Above results are consistent with the notion that only partial PEH ethylene chain segments, longer than the critical length defined by the thermal conditions, can partake in crystallization.¹

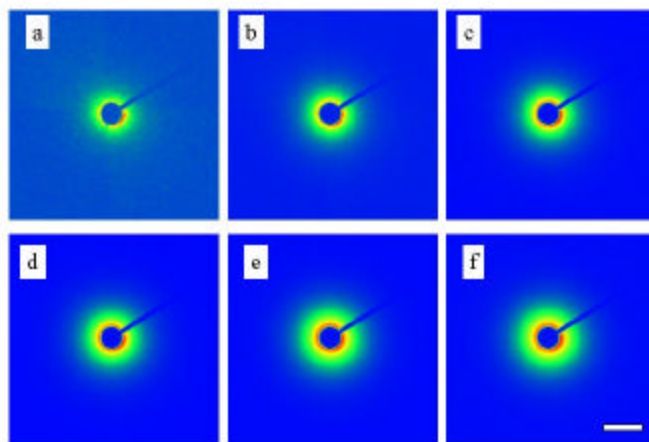


Figure 1. Selected time-resolved SAXS patterns during crystallization of PEH at 115 °C: (a) 15 s; (b) 45 s; (c) 75 s; (d) 150 s; (e) 750 s; (f) 1500 s. The white bar in (f) corresponds to the scattering vector q of 0.03 Å⁻¹.

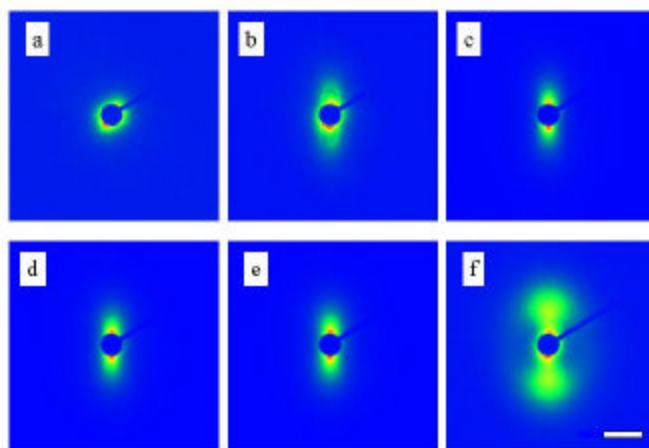


Figure 2. Selected time-resolved SAXS patterns during crystallization of PEH at 115 °C after a step shear: (a) 135 s; (b) 165 s; (c) 180 s; (d) 300 s; (e) 1050 s; (f) sample cooled to 70 °C. The shear direction is vertical. The white bar in (f) corresponds to the scattering vector q of 0.03 Å⁻¹.

It is seen in Figure 2 that the SAXS patterns are oriented along the meridional direction. The total scattering intensity is found to increase immediately upon cessation of the step shear. The rate of the increase is about

the same as crystallization under the quiescent state. However, the patterns indicate that a substantial amount of anisotropic structure was stimulated by the step shear with a duration time of only 0.33 s. It is interesting to note that the orientation direction in the initial SAXS pattern (**Figure 2a**) has an approximate 30° tilt with respect to the flow direction, which is different from the subsequent SAXS patterns. The reason is still under investigation. When the sample was cooled down to 70 °C, the intensity profile shows a distinct scattering maximum along the meridian, corresponding to a long period (L_B) of ≈ 210 Å from the well-ordered lamellar stacks (**Figure 3b**).

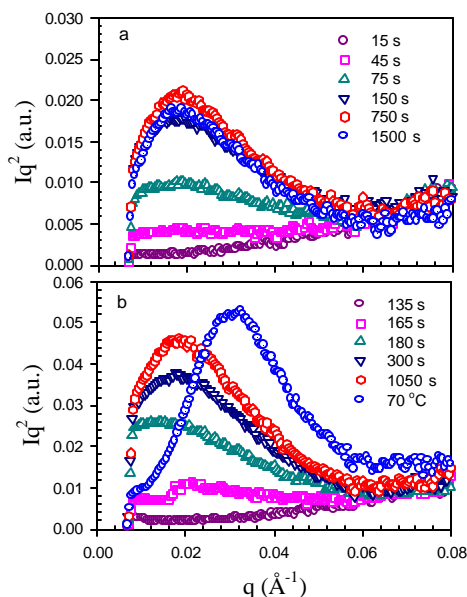


Figure 3. Selected Lorentz-corrected SAXS profiles along the meridional direction, (a) and (b) correspond to the patterns in **Figures 1** and **2**, respectively, (the standard uncertainty of Iq^2 is less than 2 % and is estimated from the relative standard deviation).

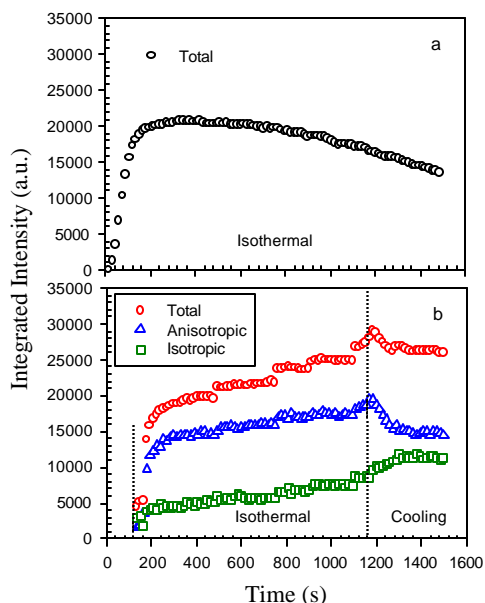


Figure 4. Evolution of total integrated SAXS intensity (Total intensity = isotropic intensity + anisotropic intensity) of PEH during isothermal crystallization at 115 °C, (a) without the step shear and (b) with step shear (the standard uncertainty of integrated intensity is less than 2 %).

In the two-dimensional SAXS pattern, the total scattering intensity can be integrated and deconvoluted into anisotropic (from oriented structures) and

isotropic (from unoriented structures) contributions, using a custom procedure developed in our laboratory.¹⁰ **Figures 4** and **5** summarize the results from this analysis. It is found that in quiescent isothermal crystallization of PEH, the total intensity is found to decrease under prolong annealing, which has been observed in other polymers.¹¹ The primary crystallization rate is rapid. Step shear at the high rate of 60 s⁻¹ and the strain of 2000 % induces a continuous increase of the total scattering intensity after primary crystallization. The rate of primary crystallization appears to be the same between shear and quiescent conditions. In addition, the oriented structures (lamellae) induced by shear seem to be generated mainly at the initial stages (primary crystallization) immediately after step shear. At the late stages, the randomly oriented lamellae, associated with the isotropic fraction, increases its contribution to the total scattering intensity (**Figure 5**). During cooling, the total scattering intensity decreases and the isotropic fraction increases significantly.

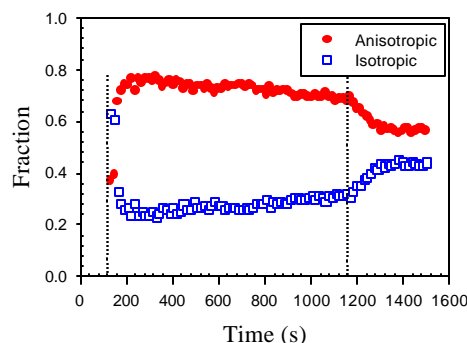


Figure 5. Evolution of the anisotropic and isotropic fractions of PEH during isothermal crystallization at 115 °C after step shear (the left and right dotted lines indicate the time of step shear and the begin of cooling, respectively, and the standard uncertainty of the fraction is less than 2 %).

Conclusions

Results from *in-situ* time-resolved SAXS measurement on PEH melt crystallization, subjected to a step shear, indicate that an oriented lamellar structure is formed at the initial crystallization stage upon cessation of the step shear. Randomly distributed lamellae are formed during the late stages. The value of long period estimated along the meridian during the shear-induced crystallization is close to that under the quiescent crystallization condition in PEH.

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